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(54) Title: CATALYST AND METHOD FOR THE CARBONYLATION OF OXIRANES

(54) Bezeichnung: KATALYSATOR UND VERFAHREN ZUR CARBONYLIERUNG VON OXIRANEN

(57) Abstract: The invention relates to the production of lactones by means of the catalytic carbonylation of oxiranes. According to the invention, the catalyst used is a catalyst system consisting of a) at least one cobalt compound as component A, and b) at least one metallic compound of general formula (I) as component B In formula (I) MX<sub>n-x</sub>, M represents an alkaline earth metal or a metal pertaining to groups 3, 4, 12 or 13 of the periodic table, R represents hydrogen or a hydrocarbon radical which can be substituted on all of the carbon atoms except the carbon atom linked to M, X represents an anion, n represents a number corresponding to the valency of M, and x represents a number between 0 and n, the selection of n and x resulting in charge neutrality.

(57) Zusammenfassung: Die Herstellung von Lactonen erfolgt durch katalytische Carbonylierung von Oxiranen, wobei ein Katalysatorsystem aus a) mindestens einer Cobaltverbindung als Komponente A und b) mindestens einer Metallverbindung der allgemeinen Formel (I) als Komponente B: MX<sub>n-x</sub> (I) mit der Bedeutung, M Erdalkalimetall oder Metall der Gruppen 3, 4 oder 12 oder 13 des Periodensystems der Elemente, R Wasserstoff oder Kohlenwasserstoffrest, der außer am mit M verbundenen Kohlenstoffatom an den Kohlenstoffatomen substituiert sein kann, X Anion, n Zahl, die der Wertigkeit von M entspricht, x Zahl im Bereich von 0 bis n, wobei n und x so gewählt sind, dass sich Ladungsneutralität ergibt, als Katalysator eingesetzt wird.

## Katalysator und Verfahren zur Carbonylierung von Oxiranen

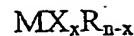
Die Erfindung betrifft die Herstellung von Lactonen durch katalytische Carbonylierung von Oxiranen in Gegenwart eines Katalysatorsystems, ein entsprechendes  
10 Katalysatorsystem und dessen Verwendung.

Die katalytische Carbonylierung von einfachen und substituierten Oxiranen ist an sich bekannt. Oft sind die Produkte nicht die erwünschten Lactone, oder die Reaktionsführung oder die Ausgangsstoffe lassen eine effiziente Herstellung oder Isolierung von Lactonen  
15 nicht zu. Häufig sind dabei die Verbindungen nur durch aufwendige und kostenintensive Synthesen zugänglich.

In der JP-A-09 169 753 ist die Carbonylierung von Epoxiden zu Lactonen in einem Durchlaufreaktor an  $\text{Co}_2\text{CO}_3$  als Katalysator beschrieben. Die Umsätze betragen nur 30%.  
20 Dies bedeutet, dass zum Erreichen einer hohen Ausbeute und Reinheit des Lactons eine Trennungs- und Rückführungseinrichtung benötigt wird.

GB-A-1,020,575 betrifft ein Verfahren zur Herstellung von Polymeren von  $\beta$ -Lactonen. Kohlenmonoxid und ein 1,2-Epoxid werden zur Bildung eines  $\beta$ -Lactons als  
25 Zwischenprodukt umgesetzt. Dabei wird Dicobaltoctacarbonyl als Katalysator eingesetzt. Zudem kann ein Promotor eingesetzt werden, der ausgewählt ist aus Metallhalogeniden wie Kaliumiodid und quarternären Ammoniumhalogeniden wie Tetraethylammoniumbromid. Die Ausbeuten an Lacton betragen jedoch weniger als 10%, die Hauptfraktionen der Produkte sind Polyhydroxypropionester. Zudem wird die Reaktion  
30 in einer komplizierten Weise mit mehreren Druckstufen gefahren.

EP-B-0 577 206 betrifft die Carbonylierung von Epoxiden an einem Katalysatorsystem aus einer Cobaltquelle und einer Hydroxy-substituierten Pyridinverbindung, insbesondere 3-Hydroxypyridin oder 4-Hydroxypyridin. Die Carbonylierung wird vorzugsweise in



(I)

5

mit der Bedeutung

M Erdalkalimetall oder Metall der Gruppen 3, 4 oder vorzugsweise 12  
oder 13 des

10 R Periodensystems der Elemente,  
Wasserstoff oder Kohlenwasserstoffrest, der außer am mit M  
verbundenen  
Kohlenstoffatom an den Kohlenstoffatomen substituiert sein kann,

X Anion

n Zahl, die der Wertigkeit von M entspricht,

15 x Zahl im Bereich von 0 bis n,

wobei n und x so gewählt sind, dass sich Ladungsneutralität ergibt,

als Katalysator eingesetzt wird.

20 Die Erfindung wird ferner gelöst durch einen wie vorstehend definierten Katalysator, mit Ausnahme der Kombination  $Al(C_2H_5)_3/Co(acac)_3$ .

25 Das Katalysatorsystem  $Al(C_2H_5)_3/Co(acac)_3$  ist bereits in Die Makromolekulare Chemie 89, 1965, Seiten 263 bis 268 beschrieben. Die Literaturstelle befasst sich mit der Copolymerisation von Kohlenmonoxid mit Alkylenoxiden. Die Bildung von Lactonen wird nicht beschrieben.

30 Lactone sind wertvolle Verbindungen zur Herstellung von bioabbaubaren Polyestern, s. beispielsweise EP-A-0 688 806. Diese Polyester finden vielfältige Anwendung, beispielsweise als Polyol bei der Polyurethanherstellung oder als Werkstoff.

35 Es wurde erfindungsgemäß gefunden, dass eine Kombination von Cobaltverbindungen, insbesondere in einem niedrigen Oxidationszustand, und Metallverbindungen für die schonende Carbonylierung von Oxiranen zu Lactonen ein effizientes Katalysatorsystem bilden.

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Amine, Amide, Phosphane, Nitro- oder Nitril- etc. Funktionalitäten. Donor L kann auch ein Olefin oder Aromat sein.

Selbstverständlich können auch Mischungen von mehreren unterschiedlichen  
5 Komponenten B und/oder A als Katalysatorsystem benutzt werden.

Besonders bevorzugt ist die Kombination von Dicobaltoctacarbonyl und  
Trimethylaluminium oder Dicobaltoctacarbonyl und Triethylaluminium oder  
Dicobaltoctacarbonyl und Tri(sec-Butyl)aluminium, oder Dicobaltoctacarbonyl und  
10 Trisisopropoxyaluminium.

Die Carbonylierung wird im Allgemeinen unter erhöhtem Druck und bei erhöhter  
Temperatur durchgeführt. Allerdings wird auch bei einem Kohlenmonoxiddruck von einer  
Atmosphäre Produktbildung beobachtet. Der Druck wird im Allgemeinen generiert durch  
15 CO-Gas. Dieser Druck kann in bestimmten Fällen auch partial durch ein inertes Medium  
wie Argon, Stickstoff generiert werden. Die Drücke liegen dabei zwischen 1 und 250 bar,  
bevorzugt zwischen 10 und 100 bar, besonders bevorzugt zwischen 20 und 60 bar. Die  
Reaktion kann allgemein bei Temperaturen zwischen -10 und 200 °C durchgeführt werden.  
Die bevorzugte Temperatur liegt zwischen 20 und 150 °C, besonders bevorzugt zwischen  
20 40 und 110 °C.

Die Carbonylierung von Epoxiden kann sowohl absatzweise als auch in einem  
kontinuierlichen Verfahren durchgeführt werden. Sie kann sowohl in der Gasphase als  
auch in einem inerten Reaktionsmedium durchgeführt werden. Dieses Medium ist im  
25 Allgemeinen eine Flüssigkeit. Diese sind übliche Lösungsmittel wie Ether, Diglyme,  
Triglyme, Tetraglyme, Tetrahydrofuran, Dimethoxyethan, Kohlenwasserstoffe wie Hexan,  
Octan, Isopar, Benzol, Toluol, Xylol, Decalin; chlorierte Kohlenwasserstoffe wie  
Dichlormethan, Dichlorethan, Dichlorbenzol oder polare Lösungsmittel wie DMF, DMSO,  
Ester, Nitrile, Nitroverbindungen, Ketone oder sogenannte ionische Flüssigkeiten.  
30 Bevorzugte Lösungsmittel sind DME, Diglyme, Dichlormethan. Auch kann das Oxiran als  
Reaktionsmedium verwendet werden.

Zur weiteren Aktivierung des Katalysatorsystems können Donorliganden hinzugegeben  
werden, wie Phosphane oder Nitrile. Indem man die Katalysatorkomponenten (z.B. Cobalt  
35 und Alkylverbindung) auf ein partikuläres Trägermaterial, z.B. Silica oder Aluminiumoxid

Bevorzugt verwendet man als Oxiranverbindung Ethylenoxid, Propylenoxid, Butylenoxid (1-Butenoxid, BuO), Cyclopentenoxid, Cyclohexenoxid (CHO), Cycloheptenoxid, 2, 3-Epoxypropylphenylether, Epichlorhydrin, Epibromhydrin, i-Butenoxid (IBO), Styroloxid oder Acryloxide. Besonders bevorzugt verwendet man Ethylenoxid (EO), Propylenoxid (PO), Butylenoxid oder i-Butenoxid, ganz besonders bevorzugt Ethylenoxid und Propylenoxid oder deren Mischungen.

- Die für das erfindungsgemäße Verfahren zu verwendenden Oxiranverbindungen können z.B. über dem Fachmann bekannte Epoxidierungen von endständigen Olefinen gewonnen werden. Verläuft die Epoxidierung stereounspezifisch, so ist eine Racematspaltung vorzunehmen. Methoden zur Racematspaltung, z.B. mittels HPLC-Chromatographie mit chiralem Säulenmaterial, sind dem Fachmann bekannt. Vorteilhafterweise stellt man die Oxiranverbindung ausgehend von einem endständigen Olefin über etablierte stereoselektive Verfahren unmittelbar in enantiomerreiner oder in optisch angereicherter Form dar. Ein geeignetes Verfahren ist z.B. die so genannte Sharpless-Epoxidierung (s. auch J. Am. Chem. Soc. 1987 (109), S. 5765 ff. und 8120 ff.; sowie "Asymmetric Synthesis", Hrsg. J.D. Morrison, Academic Press, New York, 1985, Band 5, Kapitel 7 und 8).
- Des weiteren gelangt man über bei Jacobsen et al., Tetrahedron Lett. 1997, 38, Seiten 773 bis 776; und J. Org. Chem. 1998, 63, Seiten 6776 bis 6777, beschriebene Verfahren, die auch großtechnisch einfach durchzuführen sind, ausgehend von endständigen Olefinen bzw. racemischen terminalen Epoxiden zu optisch angereicherten Oxiranverbindungen (siehe auch Acc. Chem. Res. 2000, 33, Seiten 421 bis 431).
- Es ist auch möglich, optisch angereicherte Oxiranverbindungen dadurch herzustellen, dass man zur enantiomerreinen Oxiranverbindung das Racemat in entsprechender Menge beimengt.
- Als Verbindungen mit endständiger Doppelbindung kommen grundsätzlich alle Olefine dieser Verbindungsklasse in Betracht, z.B. Propen, 1-Buten, 1-Penten, 1-Hexen, 1-Hepten oder 1-Octen.
- Im Allgemeinen geht man bei der Reaktionsführung so vor, dass zunächst die Cobaltkomplexe (A) und die z.B. Alkylverbindungen (B) einzeln, gleichzeitig oder vorgemischt, gegebenenfalls unter Kühlung, in das Reaktionsgefäß gegeben werden. Auch

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durchgeführt. Für Online-IR Untersuchungen zur Ermittlung der Reaktionskinetik wurde mit einem ReactIR™ (SiComp™ Dippersystem) von Mettler Toledo in einem 250 ml Büchi Reaktor gearbeitet.

5 **Allgemeine Verfahrensweise:**

Zu Dicobaltoctacarbonyl  $\text{Co}_2\text{CO}_8$  (1 äq.) in Diglyme gab man bei 0 °C unter einer Argonatmosphäre die gewünschte Menge an Epoxid (s.a. Tabellen 1 bis 4). Abschließend wurde eine Verbindung des Typs B (1-6 äq.) zugegeben (s.a. Tabelle 1 bis 4).

10 Zur Befüllung des Stahlautoklaven (100 oder 250 ml) wurde zunächst evakuiert, die Beschickung erfolgte unter Argon-Gegenstrom. Nach Überführung in den Stahlautoklaven wurde ein Kohlenmonoxiddruck von 10-65 bar eingestellt, und die Carbonylierung wurde über einen vorgegebenen Zeitraum bei Temperaturen von 75 - 105 °C gehalten. Die Carbonylierung wurde durch Druckverminderung auf Umgebungsdruck abgebrochen, die erhaltene Reaktionslösung nach Abkühlen auf 0 °C aus dem Autoklaven entnommen und analysiert. Zur Katalysatorabtrennung kann die erhaltene Lösung in ein Gemisch aus Diethylether/Pentan gegeben werden. Durch Filtration über Kieselgel werden der Katalysator sowie geringste Polymeranteile abgetrennt, eine anschließende destillative Trennung des Filtrats ergibt das Lacton in Reinform.

20 Die Erfindung wird durch die nachstehenden Beispiele näher erläutert.

**Beispiele**

25 **Beispiel 1:**

Dicobaltoctacarbonyl  $\text{Co}_2\text{CO}_8$  (260 mg) wird in 16 ml Diglyme gelöst, die Lösung wird auf 0 °C gekühlt, und 8 ml Propylenoxid werden zugefügt. Nach Zugabe von 0,77 ml einer 2N Lösung von  $\text{Me}_3\text{Al}$  in Toluol wird die Reaktionslösung unter Ausschluss von Feuchtigkeit und Sauerstoff in einen 100 ml Stahlautoklaven mit Glashülse überführt. Die Carbonylierungsreaktion wird für 5 Stunden unter 60 bar CO bei 75 °C durchgeführt. Der Abbruch der Carbonylierungsreaktion erfolgt durch Druckverminderung auf Umgebungsdruck und Kühlung auf 0 °C. Die Analyse ( $^1\text{H}$ - und  $^{13}\text{C}$ -NMR) einer entnommenen Probe ergibt eine vollständige Carbonylierung des Epoxids und einen Lactonanteil von >95% (Nebenprodukte sind Polyhydroxybutyrat und Aceton).

Feuchtigkeit und Sauerstoff in einen 100 ml Stahlautoklaven mit Glashülse überführt. Die Carbonylierungsreaktion wird für 16 Stunden unter 60 bar CO bei 75 °C durchgeführt. Der Abbruch der Carbonylierungsreaktion erfolgt durch Druckverminderung auf Umgebungsdruck und Kühlung auf 0 °C. Die Analyse (<sup>1</sup>H- und <sup>13</sup>C-NMR) einer entnommenen Probe ergibt eine nahezu vollständige Carbonylierung des Epoxids und einen Lactonanteil von > 85% (Nebenprodukte sind Polyhydroxybutyrat und Aceton).

In der nachfolgenden Tabelle werden weitere Experimente zusammengefasst, die zeigen, dass hohe Umsätze in kurzer Zeit mit diversen Kombinationen von Cobaltverbindungen und Komponente B erzielt werden.

**Tabelle 1: Variation der Al-Komponente**

Nr.	Katalysator	Epoxid	Reaktionsbedingungen	Ausbeute
15	Co <sub>2</sub> CO <sub>8</sub> (1äq.) Me <sub>3</sub> Al (2äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/ 5h	Umsatz 100% Lacton 96%
20	Co <sub>2</sub> CO <sub>8</sub> (1äq.) Et <sub>3</sub> Al (2äq.)	PO (160äg.)	75 °C/ 60 bar CO/ Diglyme/ 5h	Umsatz 100% Lacton 91%
25	Co <sub>2</sub> CO <sub>8</sub> (1äq.) (i-Butyl) <sub>3</sub> -Al (2äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/ 5h	Umsatz 100% Lacton 87%
30	Co <sub>2</sub> CO <sub>8</sub> (1äq.) Me <sub>3</sub> Al (4äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/ 4h	Umsatz 100% Lacton 92%
35	Co <sub>2</sub> CO <sub>8</sub> (1äq.) Me <sub>3</sub> Al (6äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/ 3h	Umsatz 100% Lacton 88%
	Co <sub>2</sub> CO <sub>8</sub> (1äq.) EtCl <sub>2</sub> Al (2äq.)	PO (160 äq.)	75 °C/ 60 bar CO/ Diglyme/ 5h	Umsatz 100% Lacton 85%
	Co <sub>2</sub> CO <sub>8</sub> (1äq.) Et <sub>2</sub> ClAl ClEt <sub>2</sub> Al (1äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/5 h	Umsatz 100% Lacton 90%
	Co <sub>2</sub> CO <sub>8</sub> (1äq.) MAO (2äq.)	PO (160äq.)	75 °C/ 60 bar CO/ Diglyme/ 20h	Umsatz 90% Lacton 80%
	Co <sub>2</sub> CO <sub>8</sub> (0,5äq.) Et <sub>4</sub> NCo(CO) <sub>4</sub> (1äq.)	PO (120äq.)	75 °C/ 60 bar CO/ Diglyme/ 16h	Umsatz 100% Lacton 87%
	(i-PrO) <sub>3</sub> Al (1äq.)			

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**Tabelle 4: Variation des Epoxid/Katalysator Verhältnisses**

Nr.	Katalysator	Epoxid	Reaktionsbedingungen	Ausbeute
5 17	Co <sub>2</sub> CO <sub>8</sub> (1äq.)	PO (300äq.)	75 °C/ 60 bar CO/ Diglyme/ 10 h	Umsatz 100% Lacton 92%
	Me <sub>3</sub> Al (2äq.)			
18	Co <sub>2</sub> CO <sub>8</sub> (1äq.)	PO (600äq.)	75 °C/ 60 bar CO/ Diglyme/ 7h	Umsatz 100% Lacton 94%
	Me <sub>3</sub> Al (4äq.)			
19	Co <sub>2</sub> CO <sub>8</sub> (1äq.)	PO (1200äq.)	75 °C/ 60 bar CO/ Diglyme/ 16 h	Umsatz 80% Lacton 90%
10	Me <sub>3</sub> Al (4äq.)			

Alle Beispiele aus Tabelle 4 wurden in einem 100 ml Stahlautoklaven mit Glashülse durchgeführt; Umsätze und Lacton-Anteile wurden mit Hilfe von NMR-Messungen aus einer entnommenen Probe ermittelt; Nebenprodukte sind Polyhydroxybutyrat und in geringen Mengen Aceton.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass in der allgemeinen Formel (I) R Wasserstoff oder C<sub>1-32</sub>-Alkyl, C<sub>2-20</sub>-Alkenyl, C<sub>3-20</sub>-Cycloalkyl, C<sub>6-18</sub>-Aryl, C<sub>7-20</sub>-Aralkyl oder C<sub>7-20</sub>-Alkaryl bedeutet, wobei außer am mit M verbundenen Kohlenstoffatom an den Kohlenstoffatomen Substituenten vorliegen können,

und/oder X Cl, Br, I, Sulfonat, Oxid, C<sub>1-32</sub>-Alkoxid oder Amid bedeutet.

- 10 5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass Komponente B AlCl<sub>x</sub>R<sub>3-x</sub> ist mit x Zahl von 0 bis 3 und R C<sub>1-6</sub>-Alkyl.
- 15 6. Katalysator, wie er in einem der Ansprüche 1 bis 5 definiert ist, mit Ausnahme der Kombination Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>/Co(acac)<sub>3</sub>.
7. Verfahren zur Herstellung von Katalysatoren nach Anspruch 6 durch Vermischen der Komponenten A und B.
- 20 8. Verwendung eines Katalysators nach Anspruch 6 in Carbonylierungsreaktionen.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP 03/08479

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/20 - B01J37/04 C07C51/12 C07C51/10 C07C67/37  
 C07D305/12 C07D303/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GETZLER Y D Y L ET AL: "SYNTHESIS OF    BETA-LACTONES: A HIGHLY ACTIVE AND    SELECTIVE CATALYST FOR EPOXIDE    CARBOXYLATION"    JOURNAL OF THE AMERICAN CHEMICAL SOCIETY,    AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC,    US,    vol. 124, no. 7, 2002, pages 1174-1175,    XP002258049    ISSN: 0002-7863    cited in the application    page 1175, left-hand column; figure 1;    examples 1,6-10; table 1</p> <p style="text-align: center;">-/-</p>	1-8

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*&\* document member of the same patent family

Date of the actual completion of the international search

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## Name and mailing address of the ISA

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FURUKAWA J ET AL: "COPOLYMERIZATION OF CARBON MONOXIDE WITH ALKYLENE OXIDE" MAKROMOLEKULARE CHEMIE, MACROMOLECULAR CHEMISTRY AND PHYSICS, HUTHIG UND WEPF VERLAG, BASEL, CH, vol. 89, 1965, pages 263-268, XP009001879 ISSN: 0025-116X cited in the application page 264; figure 2. ---	1-8
X	US 3 260 738 A (FISCHER RUDOLPH F ET AL) 12 July 1966 (1966-07-12) column 1, line 45 - line 53 column 4, line 14 - line 25 column 3, line 16 - line 17 column 4, line 63 - line 65 ---	6-8
A	DATABASE CROSSFIRE BEILSTEIN 'Online' Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Citation Number 5952122; Reaction IDs 4080694, XP002258053 abstract & KOWALCZUK M ET AL: "SYNTHESIS OF NEW GLYCIDYLOXYPROPIOLACTONES" POLISH JOURNAL OF CHEMISTRY, vol. 55, no. 9, 1981, pages 1965-1967, ---	1-8
X	US 4 620 033 A (KONDO TAKAO ET AL) 28 October 1986 (1986-10-28) *GLEICHUNG 3* column 3 -column 5; example 7 ---	6-8
X	US 6 084 124 A (SLAUGH LYNN HENRY ET AL) 4 July 2000 (2000-07-04) column 2, line 39 - line 55; claim 1 ---	6-8
A	WO 02 12161 A (HENDERSON RICHARD KEVIN ;KVAERNER PROCESS TECH LTD (GB); WALKER AN) 14 February 2002 (2002-02-14) page 5, line 17 - line 28; claims 17-20 page 10, line 32 -page 11, line 6 ---	1-8
P,X	WO 03 050154 A (CORNELL RES FOUNDATION INC) 19 June 2003 (2003-06-19) page 26, last paragraph -page 27, paragraph 1; claims 1,3,5; table 4 ---	1-8

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### Catalyst for the carbonylation of oxiranes

The present invention relates to the preparation of lactones by catalytic carbonylation of 10 oxiranes in the presence of a catalyst system, to a corresponding catalyst system and to its use.

The catalytic carbonylation of simple and substituted oxiranes is known per se. The products are often not the desired lactones, or the reaction conditions or the starting 15 materials do not permit efficient preparation or isolation of lactones. The compounds can frequently be obtained by means of complicated and costly syntheses.

JP-A-09 169 753 describes the carbonylation of epoxides to lactones over  $\text{Co}_2(\text{CO})_8$  as catalyst in a flow-through reactor. The conversions are only 30%. This means that a 20 separation and recirculation facility is required to achieve a high yield and purity of the lactone.

GB-A-1,020,575 relates to a process for preparing polymers of  $\beta$ -lactones. Carbon monoxide and a 1,2-epoxide are reacted to form a  $\beta$ -lactone as intermediate. This is carried 25 out using octacarbonyldicobalt as catalyst. In addition, it is possible to use a promoter selected from among metal halides such as potassium iodide and quaternary ammonium halides such as tetraethylammonium bromide. However, the yields of lactone are less than 10% and the main fractions of the products are polyhydroxypropionic esters. In addition, the reaction is carried out in a complicated manner using a plurality of pressure stages.

EP-B-0 577 206 relates to the carbonylation of epoxides over a catalyst system comprising 30 a cobalt source and a hydroxy-substituted pyridine compound, in particular 3-hydroxypyridine or 4-hydroxypyridine. The carbonylation is preferably carried out in the presence of a hydroxy compound such as water or alcohols. The activities of the catalysts used are relatively low, and isolation of the lactones is not described. It has also been 35 observed that a change in the reaction mixture occurs after the carbonylation has ended.

Over a period of 24 hours, polymerization of the lactone takes place. This indicates that the lactone is not unreactive in the reaction mixture. It is also known that lactones can polymerize in the presence of pyridines.

5 Chemistry Letters 1980, pages 1549 to 1552, relates to the reaction of epoxides with carbon monoxide over a rhodium complex as catalyst. The yields are not more than 70%.

J. Org. Chem. 2001, 66, pages 5424 to 5426, describes the synthesis of  $\beta$ -lactones by carbonylation of epoxides over cobalt and Lewis acid catalysts. A system comprising 10  $\text{PPNCo}(\text{CO})_4$  and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is used as catalyst. The yields are in the range from 7 to 86%. However, the reaction time is from 7 to 24 hours, and the use of large amounts of catalyst is necessary.

J. Am. Chem. Soc. 124, No. 7, 2002, pages 1174 to 1175, describes the preparation of  $\beta$ -lactones by carbonylation of epoxides. The catalyst used is a mixture of a salt of aluminum salts and a tetracarbonylcobaltate. The handling and synthesis of the aluminum compound are complicated, so that the process cannot be carried out on a large industrial scale.

It is an object of the present invention to provide an uncomplicated and efficient process 20 for preparing lactones by carbonylation of epoxides. A further object is to provide a suitable catalyst system for this reaction.

We have found that this object is achieved by a process for preparing lactones by catalytic carbonylation of oxiranes, wherein a catalyst system comprising

- 25
- a) at least one cobalt compound as component A and
  - b) at least one metal compound of the formula (I) as component B,



(I)

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where

- M is an alkaline earth metal or a metal of group 3, 4 or preferably 12 or 35 13 of the Periodic Table of the Elements,  
R is hydrogen or a hydrocarbon radical which may be substituted on the carbon atoms other than the carbon atom bound to M,

- X is an anion,
- n is a number corresponding to the valence of M and
- x is in the range from 0 to n,

5 with n and x being selected so that the compound is uncharged,

is used as catalyst.

The object of the invention is also achieved by a catalyst as defined above except for the  
10 combination  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Co}(\text{acac})_3$ .

The catalyst system  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Co}(\text{acac})_3$  has already been described in Die Makromolekulare Chemie 89, 1965, pages 263 to 268. This reference is concerned with the copolymerization of carbon monoxide with alkylene oxides and does not describe the  
15 formation of lactones.

Lactones are valuable compounds for preparing biodegradable polyesters, cf., for example, EP-A-0 688 806. These polyesters are widely used, for example as polyols in polyurethane production or as material of construction.

20 According to the present invention, it has been found that a combination of cobalt compounds, in particular compounds in a low oxidation state, and metal compounds forms an efficient catalyst system for the carbonylation of oxiranes to lactones under mild conditions.

25 In the catalyst system used according to the present invention, preference is given to 0.1 to 1000 mol, particularly preferably from 1 to 100 mol, of component B being present per mole of component A.

30 The component A is preferably selected so that a cobalt carbonyl compound is present under the reaction conditions. This means that a cobalt carbonyl compound can be used directly as component A or it is possible to use a compound which is converted into a cobalt carbonyl compound under the reaction conditions.

35 R is preferably hydrogen or  $\text{C}_{1-32}$ -alkyl,  $\text{C}_{2-20}$ -alkenyl,  $\text{C}_{3-20}$ -cycloalkyl,  $\text{C}_{6-18}$ -aryl,  $\text{C}_{7-20}$ -aralkyl or  $\text{C}_{7-20}$ -alkaryl, with substituents being able to be present on the carbon atoms other than the carbon atom bound to M. R is preferably hydrogen or a monoanionic

hydrocarbyl group, for example C<sub>1-32</sub>-alkyl such as methyl, ethyl, i- or n-propyl, i-, n- or t-butyl, n-pentyl or n-hexyl, C<sub>2-20</sub>-alkenyl such as propenyl or butenyl, C<sub>3-20</sub>-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclopentadienyl or cyclohexyl, C<sub>6-18</sub>-aryl such as phenyl or naphthyl, or C<sub>7-20</sub>-arylalkyl, e.g. benzyl (the hydrocarbyl group is preferably alkyl and particularly preferred hydrocarbyl groups are methyl or ethyl),

X is an anion such as halide (apart from fluoride), sulfonate, oxide, C<sub>1-32</sub>-alkoxide, amide; with preferred anions being halide or alkoxide, particularly preferably chloride or C<sub>1-12</sub>-alkoxide,

10 and n corresponds to the oxidation state OS or the valence of the metal and x is smaller than or equal to n and is not negative (for each oxide ligand, x = x + 1).

15 The component B is preferably AlCl<sub>x</sub>R<sub>3-x</sub> where x is from 0 to 3 and R is C<sub>1-6</sub>-alkyl. The numbers n and x can be integers or fractions. Fractions can arise in the case of a mixture of such compounds.

20 If desired, component A or B may also have an uncharged donor L bound in its coordination sphere. A donor L is in general an uncharged compound containing oxygen, nitrogen or phosphorus atoms, e.g. ethers, carbonates, ketones, sulfoxides, amines, amides, phosphines, nitro functions or nitrile functions, etc. Olefins and aromatics are also possible as donors L.

25 Of course, it is also possible to use mixtures of a plurality of different components B and/or A as catalyst system.

30 Particular preference is given to a combination of octacarbonyldicobalt and trimethylaluminum or octacarbonyldicobalt and triethylaluminum or octacarbonyldicobalt and tri(sec-butyl)aluminum, or octacarbonyldicobalt and triisopropoxyaluminum.

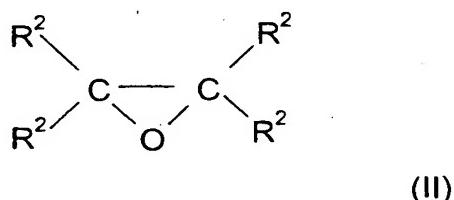
The carbonylation is generally carried out under superatmospheric pressure and at elevated temperature. However, product formation is also observed at a carbon monoxide pressure of one atmosphere. The pressure is generally generated by means of CO gas. In particular cases, the pressure can also be partially generated by means of an inert medium such as argon or nitrogen. The pressures are in the range from 1 to 250 bar, preferably from 10 to 100 bar, particularly preferably from 20 to 60 bar. The reaction can generally be carried out

at from -10 to 200°C. The preferred temperature range is from 20 to 150°C, particularly preferably from 40 to 110°C.

5 The carbonylation of epoxides can be carried out either batchwise or in a continuous process. It can be carried out either in the gas phase or in an inert reaction medium. This medium is generally a liquid. Suitable liquids are customary solvents such as ethers, diglyme, triglyme, tetraglyme, tetrahydrofuran, dimethoxyethane, hydrocarbons such as hexane, octane, isopar, benzene, toluene, xylene decalin; chlorinated hydrocarbons such as dichloromethane; dichloroethane, dichlorobenzene or polar solvents such as DMF, DMSO,  
10 esters, nitriles, nitro compounds, ketones or ionic liquids. Preferred solvents are DME, diglyme, dichloromethane. The oxirane can also be used as reaction medium.

To activate the catalyst system further, it is possible to add donor ligands such as phosphines or nitriles. Application of the catalyst components (e.g. cobalt and alkyl  
15 compound) to a particulate support material, e.g. silica or aluminum oxide, makes it possible to carry out the reaction in the absence of solvent as a gas-phase carbonylation.

Suitable oxirane compounds are ethylene oxide and substituted epoxides. These are usually compounds having the formula (II):  
20



In this formula, the radicals R<sup>2</sup> are each, independently of one another, hydrogen, halogen, a nitro group -NO<sub>2</sub>, a cyano group -CN, and ester group -COOR<sup>3</sup> or a hydrocarbon group having from 1 to 32 carbon atoms which may be substituted. The radicals R<sup>2</sup> in a compound (II) can all be the same, some of them can be the same or they can be four different radicals. R<sup>3</sup> can be C<sub>1-12</sub>-alkyl or aryl.  
25

Use is preferably made of geminally substituted epoxides, particularly preferably epoxides substituted only in the 1 position.  
30

Examples of suitable hydrocarbon groups are C<sub>1-32</sub>-alkyl such as methyl, ethyl, i- or n-propyl, i-, n- or t-butyl, n-pentyl or n-hexyl, C<sub>2-20</sub>-alkenyl such as propenyl or butenyl, C<sub>3-20</sub>-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, C<sub>6-18</sub>-aryl such

as phenyl or naphthyl, and C<sub>7-20</sub>-arylalkyl, e.g. benzyl. It is also possible for two radicals R<sup>2</sup> located on different carbon atoms of the epoxy group to be joined to one another so as to form a C<sub>3-20</sub>-cycloalkylene group.

- 5 Substituents which may be present on the C<sub>1-32</sub>-hydrocarbon group or R above can be, in particular, the following groups: halogen, cyano, nitro, thioalkyl, tert-amino, alkoxy, aryloxy, arylalkyloxy, carbonyldioxyalkyl, carbonyldioxyaryl, carbonyldioxyarylalkyl, alkoxycarbonyl, aryloxycarbonyl, arylalkyloxycarbonyl, alkylcarbonyl, arylcarbonyl, arylalkylcarbonyl, alkylsulfinyl, arylsulfinyl, arylalkylsulfinyl, alkylsulfonyl, arylsulfonyl and arylalkylsulfonyl.

10 The oxirane compound used is preferably ethylene oxide, propylene oxide, butylene oxide (1-butene oxide, BuO), cyclopentene oxide, cyclohexene oxide (CHO), cycloheptene oxide, 2,3-epoxypropyl phenyl ether, epichlorohydrin, epibromohydrin, i-butene oxide (IBO), styrene oxide or an acryl oxide. Particular preference is given to using ethylene oxide (EO), propylene oxide (PO), butylene oxide or i-butene oxide, very particularly 15 preferably ethylene oxide or propylene oxide or a mixture thereof.

20 The oxirane compounds to be used for the process of the present invention can be obtained, for example, by epoxidation of terminal olefins using methods known to those skilled in the art. If the epoxidation occurs stereounspecifically, resolution of the racemate has to be carried out. Methods of resolving racemates, e.g. by means of HPLC chromatography using a chiral column material, are known to those skilled in the art. The oxirane compound is advantageously prepared directly in enantiomerically pure or optically 25 enriched form from a terminal olefin by means of established stereoselective processes. A suitable process is, for example, the Sharpless epoxidation (cf. J. Am. Chem. Soc. 1987 (109), p. 5765 ff. and 8120 ff.; and "Asymmetric Synthesis", Edited by J.D. Morrison, Academic Press, New York, 1985, Volume 5, Chapters 7 and 8).

30 Furthermore, optically enriched oxirane compounds can be obtained from terminal olefins or racemic terminal epoxides by the methods described in Jacobsen et al., Tetrahedron Lett. 1997, 38, pages 773 to 776; and J. Org. Chem. 1998, 63, pages 6776 to 6777, which are also simple to carry out on a large industrial scale (see also Acc. Chem. Res. 2000, 33, pages 421 to 431).

35 It is also possible to prepare optically enriched oxirane compounds by mixing an appropriate amount of the racemate with the enantiomerically pure oxirane compound.

As compounds having a terminal double bond, it is in principle possible to use all olefins of this class of compound, e.g. propene, 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene.

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In general, the cobalt complexes (A) and the, for example, alkyl compounds (B) are firstly introduced into the reaction vessel either individually, simultaneously or in premixed form, if appropriate with cooling. It is also possible, if desired, for the oxirane compound to be mixed into the solution/suspension of the catalyst components before the latter is

10 transferred to the reaction vessel. Furthermore, the oxirane compound can also be introduced directly into the reaction vessel. The carbonylation is preferably carried out under inert conditions, i.e. in the absence of moisture and air.

15 Termination of the reaction and separation and purification of the lactones can be carried out by generally known methods. For example, the lactone can be isolated in a simple fashion by distillation or crystallization.

20 The process of the present invention enables 3-hydroxypropiolactones to be obtained from the corresponding enantiomerically pure oxirane compounds. If these oxirane compounds are used in optically enriched form, lactones in which the degree of optical purity corresponds directly to the degree in the oxirane are obtained. Lactones prepared in this way can be used to establish the thermoplastic property profile of the biodegradable polymers, whose properties can be set very simply and specifically for desired applications.

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The advantages of the invention can be seen in the simple operation and in the high activity and productivity of the carbonylation catalysts and the commercially available catalyst components.

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The present invention also provides a process for preparing the catalyst used according to the present invention by mixing the components A und B. The invention further relates to the use of the catalyst in carbonylation reactions.

### Reagents

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The reagents used came from Fluka, Aldrich or Merck and were used without further purification. The solvents were dried over molecular sieves and in each case degassed before use. The aluminum alkyl compounds were used as solutions in toluene.

### Analysis

NMR spectra were recorded on a Bruker AMX400 spectrometer. The IR measurements (KBr or directly as solution) were carried out on Bruker IFS 113V and IFS 66V instruments. For on-line IR studies to determine the reaction kinetics, a ReactIR™ (SiComp™ Dippersystem) from Mettler Toledo in a 250 ml Büchi reactor was employed.

### General procedure:

The desired amount of epoxide (cf. Tables 1 to 4) was added to octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (1 eq.) in diglyme at 0°C under an argon atmosphere. A compound of type B (1-6 eq.) was finally added (cf. Tables 1 to 4).

To charge the steel autoclave (100 or 250 ml), it was firstly evacuated and then charged under a countercurrent of argon. After the starting materials had been transferred to the steel autoclave, a carbon monoxide pressure of 10-65 bar was set and the carbonylation mixture was maintained at 75-105°C for a prescribed period. The carbonylation was stopped by reducing the pressure to ambient pressure, and the reaction solution obtained was cooled to 0°C, taken from the autoclave and analyzed. To separate off the catalyst, the resulting solution can be introduced into a mixture of diethyl ether/pentane. The catalyst and traces of polymer are separated off by filtration through silica gel, and subsequent fractional distillation of the filtrate gives the lactone in pure form.

Die Erfindung wird durch die nachstehenden Beispiele näher erläutert.

### Examples

#### Example 1:

Octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (260 mg) is dissolved in 16 ml of diglyme, the solution is cooled to 0°C and 8 ml of propylene oxide are added. After addition of 0.77 ml of 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the reaction mixture is transferred in the absence of moisture and oxygen to a 100 ml steel autoclave provided with a glass liner. The carbonylation reaction is carried out at 75°C under 60 bar of CO for 5 hours. The carbonylation reaction is stopped by reducing the pressure to ambient pressure and cooling to 0°C. Analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a sample indicates complete carbonylation of the epoxide and a lactone yield of > 95% (by-products are polyhydroxybutyrate and acetone).

#### Example 2:

In a 250 ml steel autoclave provided with an IR probe, octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (780 mg) are dissolved in 50 ml of diglyme at 0°C under argon, and 26 ml of propylene oxide are added. After addition of 7 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the autoclave is pressurized with 60 bar of CO. The carbonylation reaction is carried out at 95°C under 5 60 bar of CO for 2 hours. The carbonylation reaction is stopped by reducing the pressure to ambient pressure and cooling to 0°C. Analysis ( $^1\text{H}$ - and  $^{13}\text{C-NMR}$ ) of a sample indicates complete carbonylation of the epoxide and a lactone yield of > 95% (by-products are polyhydroxybutyrate and acetone).

10 Example 3:

In a 250 ml steel autoclave provided with an IR probe, octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (780 mg) are dissolved in 50 ml of diglyme at 0°C under argon, and 26 ml of propylene oxide are added. After addition of 7 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the autoclave is pressurized with 10 bar of CO. The carbonylation reaction is carried out at 75°C under 15 10 bar of CO for 4 hours. To stop the reaction, the pressure is brought down to ambient pressure and the mixture is cooled to 0°C. Analysis ( $^1\text{H}$ - and  $^{13}\text{C-NMR}$ ) of a sample indicates complete carbonylation of the epoxide and a lactone yield of > 95% (by-products are polyhydroxybutyrate and acetone).

20 Example 4:

Octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (130 mg) is dissolved in 8 ml of diglyme, the solution is cooled to 0°C and 7 ml of butyloxirane are added. After addition of 0.39 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the reaction solution is transferred in the absence of moisture and oxygen to a 100 ml steel autoclave provided with a glass liner. The carbonylation 25 reaction is carried out at 75°C under 60 bar of CO for 14 hours. The carbonylation reaction is stopped by reducing the pressure to ambient pressure and cooling to 0°C. Analysis ( $^1\text{H}$ - and  $^{13}\text{C-NMR}$ ) of a sample indicates about 70% carbonylation of the epoxide and a proportion of lactone in the product of > 75%.

30 Example 5:

Octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  (130 mg) and tetraethylammonium tetracarbonylcobaltate  $\text{Et}_4\text{NCo}(\text{CO})_4$  (232 mg) are dissolved in 10 ml of diglyme, the solution is cooled to 0°C and 6 ml of propylene oxide are added. After addition of aluminum isopropoxide  $(i\text{-PrO})_3\text{Al}$ , the reaction solution is transferred in the absence of moisture and oxygen to a 35 100 ml steel autoclave provided with a glass liner. The carbonylation reaction is carried out at 75°C under 60 bar of CO for 16 hours. The carbonylation reaction is stopped by reducing the pressure to ambient pressure and cooling to 0°C. Analysis ( $^1\text{H}$ - and  $^{13}\text{C-NMR}$ )

of a sample indicates virtually complete carbonylation of the epoxide and a lactone yield of > 85% (by-products are polyhydroxybutyrate and acetone).

The following table summarizes further experiments which show that high conversions can be achieved in a short time using various combinations of cobalt compounds and component B.

Table 1: Variation of the Al component

No.	Catalyst	Epoxide	Reaction conditions	Yield	
1	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/ 5h	Conversion 100%	
	Me <sub>3</sub> Al (2 eq.)			Lactone 96%	
2	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100%	
	Et <sub>3</sub> Al (2 eq.)			Lactone 91%	
15	3	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100%
		(i-Butyl) <sub>3</sub> -Al (2 eq.)		Lactone 87%	
4	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/4h	Conversion 100%	
	Me <sub>3</sub> Al (4 eq.)			Lactone 92%	
5	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/3h	Conversion 100%	
20	Me <sub>3</sub> Al (6 eq.)			Lactone 88%	
6	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100%	
	EtCl <sub>2</sub> Al (2 eq.)			Lactone 85%	
7	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100%	
	Et <sub>2</sub> ClAl ClEt <sub>2</sub> Al (1 eq.)			Lactone 90%	
25	8	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/20h	Conversion 90%
		MAO (2 eq.)		Lactone 80%	
9	Co <sub>2</sub> CO <sub>8</sub> (0.5 eq.)	PO (120 eq.)	75°C/60 bar of CO/ diglyme/16h	Conversion 100%	
	Et <sub>4</sub> NCo(CO) <sub>4</sub> (1 eq.)			Lactone 87%	
30	(i-PrO) <sub>3</sub> Al (1 eq.)				

All examples in Table 1 were carried out in a 100 ml steel autoclave provided with a glass liner; conversions and proportion of lactone were determined by NMR measurements on a sample; by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Table 2: Variation of the pressure**

No.	Catalyst	Epoxide	Reaction conditions	Yield
10	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/80 bar of CO/ diglyme/5h	Conversion 100%
	Me <sub>3</sub> Al (4 eq.)		Lactone 90%	
11	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100%
	Me <sub>2</sub> Al (4 eq.)		Lactone 93%	
12	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/40 bar of CO/ diglyme/5h	Conversion 100%
	Me <sub>3</sub> Al (4 eq.)		Lactone 92%	
10	13	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/20 bar of CO/ diglyme/5h
		Me <sub>3</sub> Al (4 eq.)		Lactone 91%
14	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	75°C/10 bar of CO/ diglyme/5h	Conversion 100%
	Me <sub>3</sub> Al (4 eq.)		Lactone 92%	

15 All examples in Table 2 were carried out in a 250 ml steel autoclave without glass liner and with monitoring of the reaction by IR; conversions and proportions of lactone were determined by NMR measurements on a sample; by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Table 3: Variation of the temperature**

No.	Catalyst	Epoxide	Reaction conditions	Yield
15	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	95°C/60 bar of CO/ diglyme/2h	Conversion 100%
	Me <sub>3</sub> Al (4 eq.)		Lactone 92%	
25	16	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (160 eq.)	105°C/60 bar of CO/ diglyme/1h
		Me <sub>3</sub> Al (4 eq.)		Lactone 91%

All examples in Table 3 were carried out in a 250 ml steel autoclave without glass liner and with monitoring of the reaction by IR.; conversions and proportions of lactone were determined by NMR measurements on a sample; by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Table 4: Variation of the epoxide/catalyst ratio**

No.	Catalyst	Epoxide	Reaction conditions	Yield
17	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (300 eq.)	75°C/60 bar of CO/ diglyme/10h	Conversion 100%
5	Me <sub>3</sub> Al (2 eq.)			Lactone 92%
18	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (600 eq.)	75°C/60 bar of CO/ diglyme/7h	Conversion 100%
	Me <sub>3</sub> Al (4 eq.)			Lactone 94%
19	Co <sub>2</sub> CO <sub>8</sub> (1 eq.)	PO (1200 eq.)	75°C/60 bar of CO/ diglyme/16h	Conversion 80%
	Me <sub>3</sub> Al (4 eq.)			Lactone 90%

10

All examples in Table 4 were carried out in a 100 ml steel autoclave provided with a glass liner; conversions and proportions of lactone were determined by NMR measurements on a sample; by-products are polyhydroxybutyrate and, in small amounts, acetone.

We claim:

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1. A process for preparing lactones by catalytic carbonylation of oxiranes, wherein a catalyst system comprising

10 a) at least one cobalt compound as component A and

b) at least one metal compound of the formula (I) as component B,



(I)

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where

M is an alkaline earth metal or a metal of group 3, 4 or preferably 12 or 20 13 of the Periodic Table of the Elements,

R is hydrogen or a hydrocarbon radical which may be substituted on the carbon atoms other than the carbon atom bound to M,

X is an anion,

n is a number corresponding to the valence of M and

x is in the range from 0 to n,

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with n and x being selected so that the compound is uncharged,

is used as catalyst.

30

2. A process as claimed in claim 1, wherein the component A is selected so that a cobalt carbonyl compound is present under the reaction conditions.

3. A process as claimed in claim 1 or 2, wherein M in the formula (I) is Al, Mg, Zn or Sn.

35

4. A process as claimed in any of claims 1 to 3, wherein, in the formula (I), R is hydrogen or C<sub>1-32</sub>-alkyl, C<sub>2-20</sub>-alkenyl, C<sub>3-20</sub>-cycloalkyl, C<sub>6-18</sub>-aryl, C<sub>7-20</sub>-aralkyl or

$C_{7-20}$ -alkaryl, where substituents may be present on the carbon atoms other than the carbon atom bound to M,

and/or X is Cl, Br, I, sulfonate, oxide,  $C_{1-32}$ -alkoxide or amide.

5

5. A process as claimed in any of claims 1 to 4, wherein the component B is  $AlCl_xR_{3-x}$  where x is from 0 to 3 and R is  $C_{1-6}$ -alkyl.

10

6. ~~A catalyst as defined in any of claims 1 to 5 with the exception of the combination  $Al(C_2H_5)_3/Co(acac)_3$ .~~

7. A process for preparing catalysts as claimed in claim 6 by mixing the components A and B.

15

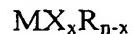
8. The use of a catalyst as claimed in claim 6 in carbonylation reactions.

### Abstract

5

Lactones are prepared by catalytic carbonylation of oxiranes using a catalyst system comprising

- 
- 10           a) at least one cobalt compound as component A and  
              b) at least one metal compound of the formula (I) as component B,



(I)

15

where

M       is an alkaline earth metal or a metal of group 3, 4 or preferably 12 or 20       13 of the Periodic Table of the Elements,

R       is hydrogen or a hydrocarbon radical which may be substituted on the carbon atoms other than the carbon atom bound to M,

X       is an anion,

n       is a number corresponding to the valence of M and

x       is in the range from 0 to n,

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with n and x being selected so that the compound is uncharged,

as catalyst.

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